Convenient diastereoselective synthesis of annulated 3-substituted-(5S*,6S*,Z)-

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Convenient Diastereoselective Synthesis of Annulated 3-substituted-(5*S**,6*S**,*Z*)-2-(2-(2,4-dinitrophenyl)hydrazono)-5,6-diphenyl-1,3-thiazinan-4-ones

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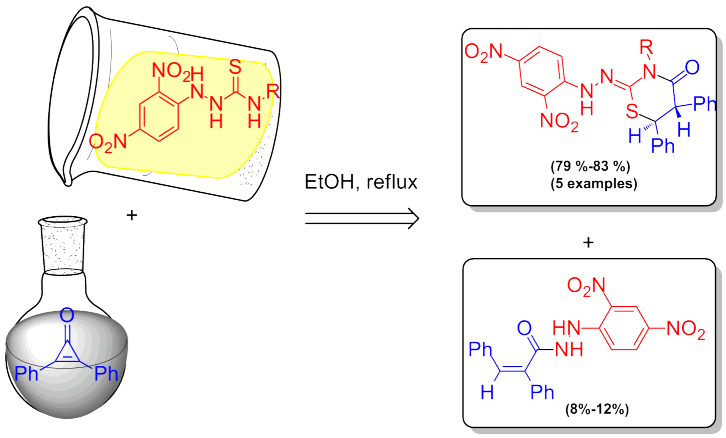

Keywords:
1,3-Thiazinan-4-ones. Substituted 2,3-diphenylacrylohydrazide. (2,4-Dinitrophenyl)-4-substituted thio-semicarbazides. 2,3-Diphenylcyclo-propenone. Annulated compounds.

Racemic 2-(2,4-dinitrophenyl)hydrazono)-5,6-diphenyl-1,3-thiazinan-4-ones and (*Z*)-*N*′-(2,4-dinitrophenyl)-2,3-diphenylacrylohydrazide were formed during the diastereoselective reaction between 4-substituted 1-(2,4-dinitrophenyl)thiosemicarbazides and 2,3-diphenylcycloprop-2-enone under refluxing ethanol. The structures of the synthesized compounds were confirmed by single crystal X-ray analyses.

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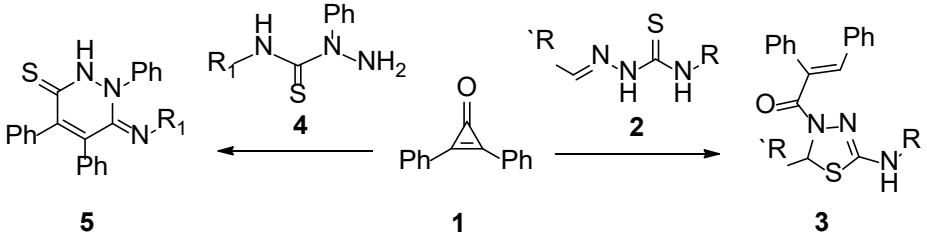
Introduction

Thiazinanones, despite being rarely reported, are very interesting compounds due to their important role in medicinal chemistry [1-3]. Substituted thiazinanones exhibited antitumor [4], antifungal activity [5] and antimalarial activity which evaluated by Kumawat et al. [6], as well as anti-oxidant activity [7]. Reactions containing an amine, carbonyl compounds and a mercapto acid in one-pot three-component condensation or a two-step process afforded thiazinanone derivatives [5]. 3-Alkyl-2-aryl-1,3-thiazinan-4-ones containing a methylsulfonyl pharmacophore were synthesized and their cyclooxygenase-2-[COX-2] inhibitory activity have been evaluated [8]. 3-Pyridin-2-ylmethyl-1,3-thiazinan-4-ones were synthesized and their anti-oxidant activities were evaluated [7].

On the other hand, the behavior of 2,3-diphenylcyclopropenone **1** towards compounds containing C=N moieties with the formation of aza-cyclopentanones (pyrrolinones) have been reported [9-12].

Due to aza-enamine reactivity shown by the reaction of alkenylidenehydrazinecarbothioamides **2** with cyclopropenone **1** and the availability of azomethine carbon as well as sulfur atom as nucleophilic sites; 3,5-disubstituted 1,3,4-thiadiazolyl-2,3-diphenylpropenones **3** were formed [13] (Scheme 1).

The reaction of **1** with various aldehyde 4-phenylthiosemicarbazones in acetic acid provided, pyrrolo[2,1-*b*]oxadiazoles [14]. Also, thione derivatives such as 2,4-disubstituted thiosemicarbazides (**4**, R = C_6H_5; $C_6H_5CH_2$) reacted with **1** *via* a nucleophilic attack of terminal-NH_2 of **4** on the carbonyl group of **1**, afforded pyridazines **5** (Scheme 1) [15].

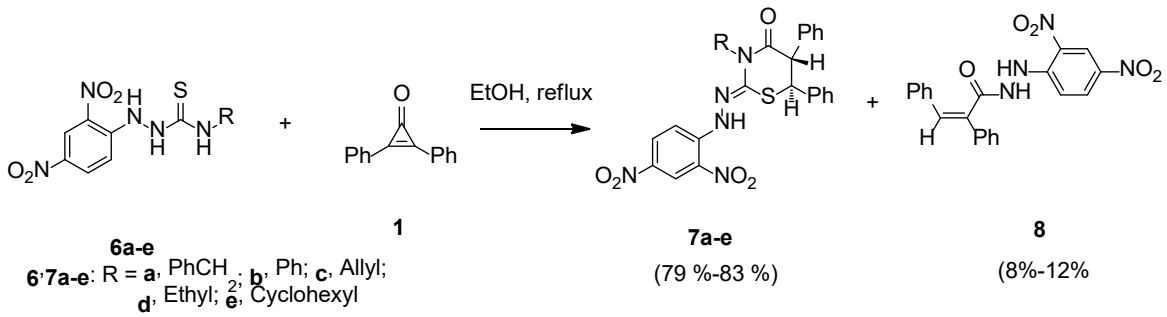


Scheme 1: Previously reported interaction of 2,3-diphenylcyclopropenone **1** with alkenylidene hydrazinecarbothioamides **2** and 2,4-disubstituted thiosemicarbazides **4**.

Optically active sulfur compounds play an important role in the biochemistry of many living organisms and are found in many synthetic drugs and bioactive natural products [16,17]. Recently, the [3+3] cyclization of amides with cyclopropenethiones afforded the formation of 6*H*-1,3-oxazin-6-ones and 6*H*-1,3-thiazin-6-ones [18].

Results and discussion

Herein, we report the reaction of 1-(2,4-dinitrophenyl)-4-substituted thiosemicarbazides **6a-e** with 2,3-diphenylcyclopropenone **1** in absolute ethanol under reflux, (5*S**,6*S**,*Z*)-2-(2-(2,4-dinitrophenyl)-hydrazono)-3-substituted-5,6-diphenyl-1,3-thiazinan-4-ones **7a-e** were precipitated as a major product (79 %-83%). The filtrate was subjected under chromatographic plates to give only one product namely, (*Z*)-*N*′-(2,4-dinitrophenyl)-2,3-diphenylacrylohydrazide **8** as a minor product (8%-12%) (Scheme 2).



Product	R	Yield (%)	Yield of **8** (%)
7a	$PhCH_2$	81	9
7b	Ph	83	8
7c	Allyl	80	10
7d	Ethyl	79	12
7e	Cyclohexyl	80	8

Scheme 2: Preparation of 2-hydrazothiazinan-4-one derivatives **7a-e** and (*Z*)-*N*′-(2,4-dinitrophenyl)-2,3-diphenylacrylohydrazide **8**.

From the structural investigation, IR spectra of **7a-e** showed the stretching frequency range between 3265-3229 cm^{-1} due to NH-stretching, 2935-2922 cm^{-1} for ali-CH, 1685-1675 cm^{-1} for C=O, 1616-1612 cm^{-1} for C=N and 1530-1524, 1344-1335 cm^{-1} due to nitro groups.

The ^1H NMR spectrum of **7a** (in $CDCl_3$) as an example showed a broad singlet at δ = 11.1 ppm due to NH-group, which was confirmed further by D_2O exchange experiment. A doublet of doublet as AX-system signals at 4.57-4.56 and 5.04-5.03 with coupling constant *J* = 4.0 Hz because of CH-6 and CH-5 of thiazinanones **7a**. The ^1H NMR spectra of **7a-e** showed the absence of any signals due to H-N^2 or H-N^4 groups of **6a-e** but compound **7a** showed a doublet of doublet signals at 5.40-5.43 and 5.64-5.61 with coupling constant 15.0 Hz for diastereotopic benzyl-CH_2 group.

The ^{13}C NMR spectrum of **7a** showed signals at δ = 47.15 and 47.90 ppm which were assigned to thiazinanone-CH6,5. Another signals at 56.36 ppm are assigned to CH_2Ph, 168.85 ppm (C=O), 146.67 ppm

(C=N) and 144.61 ppm ($(NO_2)_2$-Ar-*C*-NH). The similarities of ^{1}H NMR spectra (see experimental part) reveal that the five compounds **7a-e** belong to the same gross structure type namely 3-substituted 2-(2-(2,4-dinitrophenyl)hydrazono)-5,6-diphenyl-1,3-thiazinan-4-ones. The elemental analyses and mass spectrometry of **7a-e** clearly showed that the products were formed during the addition of one molecule of **1** to one molecule of **6a-e** without any elimination.

The X-ray crystallographic structure of compound **7a** further supported its relative configurations as (rac-5*S**,6*S**,*Z*)-3-benzyl-2-(2-(2,4-dinitrophenyl)hydrazono)-5,6-diphenyl-1,3-thiazinan-4-one. The molecular of **7a** (Figure 1 and Tables 1-7, in the crystallographic data) revealed furthermore the formation of 3-benzyl-2-(2-(2,4-dinitrophenyl)hydrazono)-5,6-diphenyl-1,3-thiazinan-4-one in the *cissiod* (*Z*) structure.

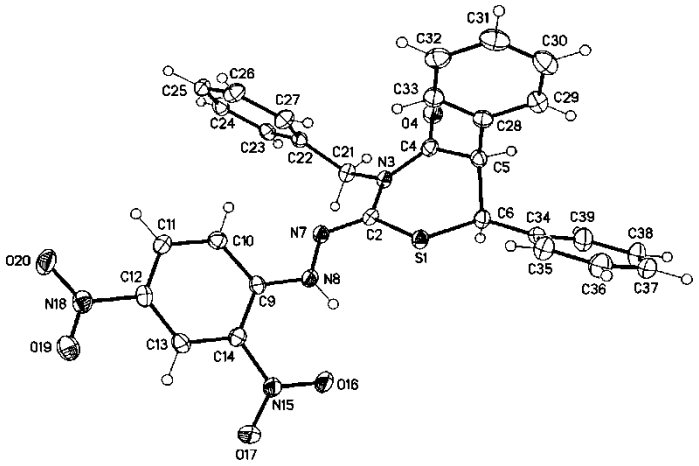


Figure 1: Molecular structure of compound **7a** (displacement parameters are drawn at 50 % probability level). The crystallographic numbering does not reflect the IUPAC numbering.

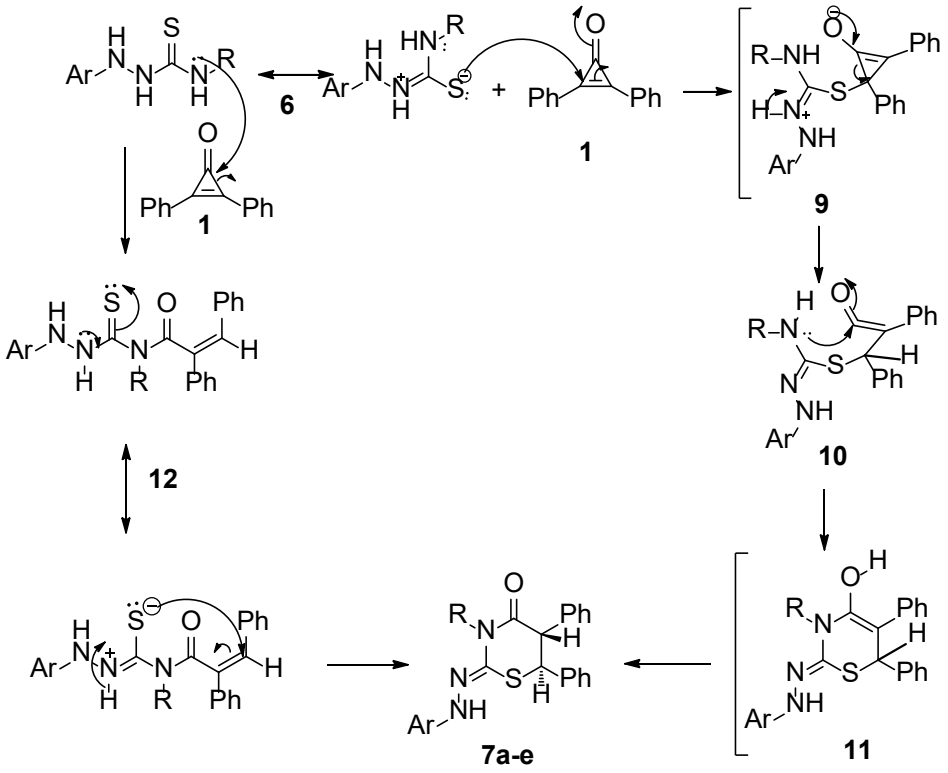
The mechanism for the formation of products **7a-e** is presented in scheme 3. The sulfur atom attacks the conjugate double bond of **1** forming the intermediate **9**. Intramolecular nucleophilic attack of N^4-H on C=O afforded the intermediate **11** which rearranged to give **7a-e** (Scheme 3). On the other hand, N^4-H attacks the carbonyl group of **1** with the formation of **7a-e** *via* intermediate **12** (Scheme 3).

The ring opening of cyclopropenones has been reported earlier by Gomaa [19] during the reaction of N^1,N^2-diarylformamidines with diphenylcyclopropenone to give 3-aryl-(*N*-4-arylformamidoyl)amino-2,3-diphenylpropionic acids.

Recently, Wu et al. reported the ring-opening acylation of cyclopropenones with organo boronic acids afforded *α*,*β*-diaryl unsaturated ketones [20].

In our study, (*Z*)-*N'*-(2,4-dinitrophenyl)-2,3-diphenylacrylohydrazide **8** was formed as a minor product (8-12%) from the reaction of **1** with **6a-e**.

The compound **8** shows IR absorption at 3320-3247 cm^{-1} due to the NH groups, strong band at 1673 cm^{-1} corresponding to carbonyl group and bands at 1528, 1344 cm^{-1} attributed to nitro groups. The ^{1}H NMR spectrum of **8** showed multiplet signals at 6.42 due to trisubstituted acrylohydrazide-CH, 9.43 (NH), in addition to the aromatic protons. In the ^{13}C NMR spectrum of **8**, the signal at δ = 165.18 was assigned to amide-CO, 145.10 due to $((NO_2)_2$-Ar-*C*-NH, 133.68 and 139.75 was attributed to acrylohydrazide C2 and C3.



Scheme 3: Mechanism for the formation of 2-hydrazothiazinan-4-one derivatives **7a-e.**

The structure of (*Z*)-*N'*-(2,4-dinitrophenyl)-2,3-diphenylacrylohydrazide **8** was determined by X-ray analysis (Figure **2**, Tables 8-15 in the supplementary data). The X-ray structure confirms the *trans (E)* geometry of the two phenyl groups with respect to the C2-C3 double bond (note that the crystallographic numbering does not correspond to the systematic IUPAC numbering rules).

The hydrazide **8** was formed *via* the nucleophilic addition of N^2-H on the C=O of **1** with the formation of intermediate **13**. Elimination of RNCS from **13** afforded the formation of **8** (Scheme 4).

In order to optimize the reaction conditions, we change the solvent of the reaction to CH_3CN or CH_2Cl_2, CH_3OH, ethyl acetate and tetrahydrofuran. However, the yields of **7a-e** decreased and in some cases such as ethyl acetate and tetrahydrofuran only traces of **7a-e** were observed detectable by TLC. The excess of one of the reaction partners, namely diphenylcyclopropenone **1** or thiosemicarbazides **6a-e**, led to a significant decrease of the yields.

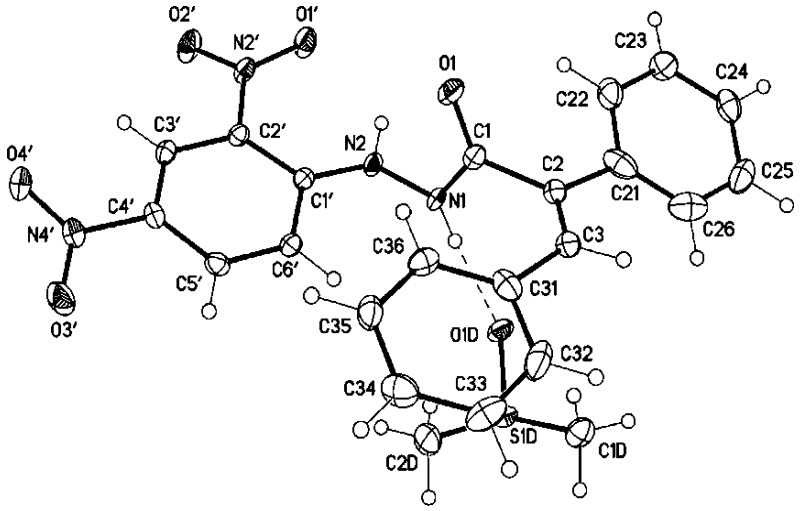
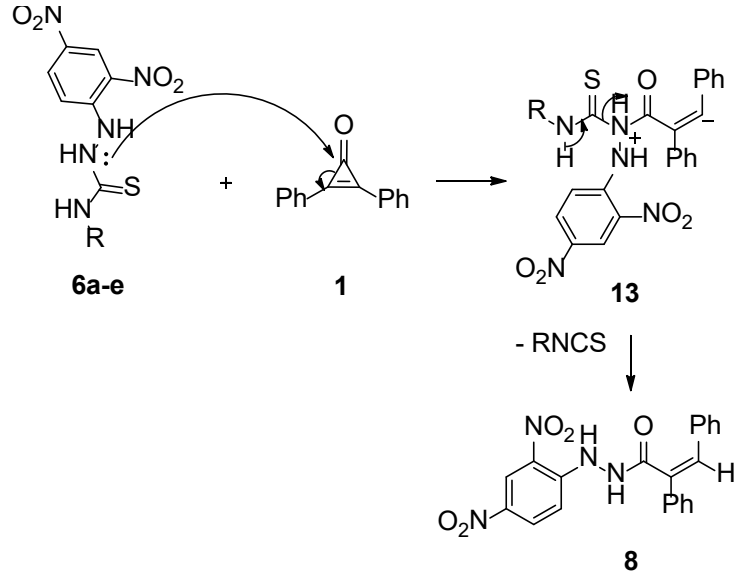


Figure 2: Molecular structure of **8** (minor disordered part and solvent omitted for clarity, displacement parameters are drawn at 50 % probability level).



Scheme 2: The plausible mechanism for the formation of (*Z*)-*N*′-(2,4-dinitrophenyl)-2,3-diphenylacrylohydrazide **8.**

Conclusion

Nucleophilic attack of dinitrophenyl-4-substituted thiosemicarbazides on 2,3-diphenylcyclopropenone afforded the formation of racemic 2-(2,4-dinitrophenyl)hydrazono)-5,6-diphenyl-1,3-thiazinan-4-ones as major products and (*Z*)-*N'*-(2,4-dinitrophenyl)-2,3-diphenylacrylohydrazide as minor product.

Experimental

Melting points were measured with Gallenkamp melting point apparatus. Infrared spectrum (IR) was recorded with Alpha, Bruker FT-IR instruments taken as KBr discs. ^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz on a Bruker AM 400 spectrometry with TMS as internal standard (δ = 0), and data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). For ^{13}C NMR, TMS (δ = 0) was used as internal standard and spectra were obtained with complete proton decoupling. Mass spectra were obtained using Finnigan MAT instrument (70 eV, EI-mode). Elemental analyses for C, H, N, and S were carried out using an Elmyer 306. Preparative layer chromatography (plc) was carried out on glass plates covered with a 1.0 mm thick layer of slurry-applied silica gel (Merck Pf_{254}).

Starting materials

The start materials **6a-e** 2-(2,4-dinitrophenyl)-*N*-substituted hydrazinecarbothioamide were prepared from the reaction between 1-(3,5-dinitrophenyl) hydrazine and the corresponding isothiocyanates in absolute ethanol under refluxing temperature according to reported literatures [21,22]. 2,3-Diphenylcycloprop-2-enone **1**) was purchased from Fluka.

General procedure:

An equimolar amounts of 2,3-diphenylcycloprop-2-enone **1** and the appropriate 1,4-disubstituted thiosemicarbazides **6a-e** were mixed in absolute ethanol and refluxed for about 4-6 h, furnished reddish orange precipitates of (5*S**,6*S**,*Z*)-2-(2-(2,4-dinitrophenyl)hydrazono)-3-substituted-5,6-diphenyl-1,3-thiazinan-4-one derivatives **7a-e** and the residue were subjected to chromatographic separation using plc and toluene/ethyl acetate (10:3) as eluent to give (*Z*)-*N'*-(2,4-dinitrophenyl)-2,3-diphenylacrylohydrazide **8** as a separated zone.

(*5S*,6S*,Z*)-3-benzyl-2-(2-(2,4-dinitrophenyl)hydrazono)-5,6-diphenyl-1,3-thiazinan-4-one (7a).

Reddish orange crystals (acetonitrile), yield 470 mg (81%), mp. 240-242 ˚C; IR (KBr) ν: 3265 (NH), 3072 (Ar-CH), 2928 (ali-CH), 1681 (C=O), 1612 (C=N), 1579 (Ar-C=C), 1530 and 1333 cm^{-1} (NO_2); ^1H NMR (400 MHz, $CDCl_3$) δ: 4.56-4.57 (dd, 1H, *J* = 4.0 Hz, thiazinanone-H6), 5.03-5.04 (dd, 1H, *J* = 4.0 Hz, thiazinanone-H5), 5.40-5.43 (d, 1H, *J* = 15.0 Hz, CH_2-benzyl), 5.61-5.64 (d, 1H, *J* = 15.0 Hz, CH_2-benzyl), 6.81-6.88 (m, 3H, Ar-H), 7.13-7.56 (m, 13H, Ar-H), 8.27-8.30 (m, 1H, Ar-H), 9.10 (m, 1H, Ar-H), 11.02 (br, 1H, hydrazo-NH); ^{13}C NMR (100MHz, $CDCl_3$) δ: 47.15 (thiazinanone-CH-6), 47.90 (thiazinanone-CH-5), 56.36 (CH_2Ph), 116.05, 123.51, 127.47, 128.01, 128.16, 128.32, 128.44, 128.67, 128.76, 129.43, 130.08, 130.25 (Ar-CH), 129.21, 132.51, 133.77, 137.05, 137.87 (Ar-C), 144.61 (Ar-*C*-NH), 146.67 (C=N), 168.85 (C=O); MS (*m/z*): 553 (M^+, 47), 462 (13), 347 (10), 207 (51), 182 (58), 149 (56), 91 (100), 77 (15); Anal. Calcd. for $C_{29}H_{23}N_5O_5S$ (553.59): C, 62.92, H, 4.19, N, 12.65, S, 5.79. Found: C, 62.79, H, 4.06, N, 12.47, S, 5.65.

(*5S*,6S*,Z*)-2-(2-(2,4-dinitrophenyl)hydrazono)-3,5,6-triphenyl-1,3-thiazinan-4-one (7b).

Reddish orange crystals (acetonitrile), yield 447 mg (83%), mp. 230-232 ˚C; IR (KBr) ν: 3262 (NH), 3076 (Ar-CH), 2932-2922 (ali-CH), 1685 (C=O), 1615 (C=N), 1577 (Ar-C=C), 1532 and 1330 cm^{-1} (NO_2); ^1H NMR (400 MHz, $CDCl_3$) δ: 4.54-4.55 (d, 1H, *J* = 4.12 Hz, thiazinanone-H6), 5.18-5.19 (d, 1H, *J* = 4.12 Hz, thiazinanone-H5), 6.80-7.00 (m, 4H, Ar-H), 7.10-7.32 (m, 9H, Ar-H), 7.35-7.52 (m, 3H, Ar-H), 8.04 (m, 1H, Ar-H), 8.98 (m, 1H, Ar-H), 10.98 (br, hydrazo-NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 47.60 (thiazinanone-CH5), 47.95 (thiazinanone-CH6), 115.97, 123.62, 127.71, 127.99, 128.39, 128.87, 129.35, 129.62, 130.08, 130.66, 131.03, 131.21 (Ar-CH), 129.35, 132.32, 133.77, 136.88, 137.86 (Ar-C), 144.57 (Ar-*C*-NH), 147.31 (C=N), 168.70 (C=O); MS (*m/z*): 539 (M^+, 62), 462 (23), 357 (48), 207 (61), 135 (37), 77 (100); Anal. Calcd. for $C_{28}H_{21}N_5O_5S$ (539.56): C, 62.33; H, 3.92; N, 12.98; S, 5.94. Found: C, 62.18; H, 3.77; N, 12.87; S, 5.86.

(*5S*,6S*,Z*)-3-allyl-2-(2-(2,4-dinitrophenyl)hydrazono)-5,6-diphenyl-1,3-thiazinan-4-one (*7c*).

Reddish orange crystals (acetonitrile), yield 402 mg (80%), mp. 208-210˚C; IR (KBr) ν: 3242 (NH), 3088 (Ar-CH), 2959-2925 (ali-CH), 1682 (C=O), 1614 (C=N), 1587 (Ar-C=C), 1529 and 1342 cm^{-1} (NO_2); ^1H NMR (400 MHz, $CDCl_3$) δ: 4.42-4.43 (d, 1H, *J* = 4.08 Hz, thiazinanone-H6), 4.70-4.92 (m, 2H, allyl-CH_2N), 4.96-4.97 (d, 1H, *J* = 4.08 Hz, thiazinanone-H5), 5.20-5.45 (m, 2H, allyl-CH_2=), 5.90-6.10 (m, 1H, allyl-CH=), 6.60-6.70 (m, 2H, Ar-H), 6.75-6.82 (m, 2H, Ar-H), 7.00-7.30 (m, 6H, Ar-H), 7.65 (m, 1H, Ar-H), 8.24 (m, 1H, Ar-H), 9.05 (m, 1H, Ar-H), 11.02 (br, 1H, hydrazo-NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ:

47.05 (allyl-CH_2N), 47.15 (thiazinanone-CH6), 47.92 (thiazinanone-CH5), 118.87 (allyl-CH_2=), 115.99, 123.60, 128.15, 128.31, 128.41, 129.24, 130.15, 130.22, 130.68 (Ar-CH), 133.75 (allyl-CH=), 128.79, 131.89, 133.69, 137.84 (Ar-C), 144.66 (Ar-*C*-NH), 146.32 (C=N), 168.43 (C=O); MS (*m/z*): 503 (M^+, 72), 457 (18), 404 (26), 207 (55), 182 (100), 99 (66), 77 (87); Anal. Calcd. for $C_{25}H_{21}N_5O_5S$ (503.53): C, 59.63; H, 4.20; N, 13.91; S, 6.37. Found: C, 59.45; H, 4.07; N, 13.74; S, 6.24.

(*5S*,6S*,Z*)-2-(2-(2,4-dinitrophenyl)hydrazono)-3-ethyl-5,6-diphenyl-1,3-thiazinan-4-one (7d).

Reddish orange crystals (acetonitrile), yield 387 mg (79%), mp. 200-202˚C; IR (KBr) ν: 3238 (NH), 3093 (Ar-CH), 2935-2923 (ali-CH), 1678 (C=O), 1616 (C=N), 1585 (Ar-C=C), 1526 and 1330 cm^{-1} (NO_2); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.35 (t, 3H, *J* = 7.77 Hz, CH_3), 4.15-4.18 (q, 2H, *J* = 7.77 Hz, CH_2), 4.45-4.46 (d, 1H, *J* = 4.10 Hz, thiazinanone-H6), 4.96-4.97 (d, 1H, *J* = 4.10 Hz, thiazinanone-H5), 6.64-6.70 (m, 2H, Ar-H), 6.76-6.81 (m, 2H, Ar-H), 7.06-7.09 (m, 6H, Ar-H), 7.68 (m, 1H, Ar-H), 8.30 (m, 1H, Ar-H), 9.03 (m, 1H, Ar-H), 11.04 (br, 1H, hydrazo-NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.86 (CH_3), 29.06 (CH_2), 47.20, 47.70 (thiazinanone-CH6,5), 116.11, 123.63, 128.00, 128.30, 128.79, 129.22, 129.78, 130.10, 130.47 (Ar-CH), 129.12, 133.43, 133.80, 134.00, 137.87 (Ar-C), 144.62 (Ar-*C*-NH), 146.63 (C=N), 168.60 (C=O); MS (*m/z*): 491 (M^+, 48), 462 (27), 445 (35), 402 (19), 182 (100), 87 (70), 77 (91); Anal. Calcd. for $C_{24}H_{21}N_5O_5S$ (491.52): C, 58.65; H, 4.31; N, 14.25; S, 6.52. Found: C, 58.51; H, 4.20; N, 14.07; S, 6.38.

(*5S*,6S*,Z*)-3-cyclohexyl-2-(2-(2,4-dinitrophenyl)hydraz-ono)-5,6-diphenyl-1,3-thiazin-an-4-one (7e).

Reddish orange crystals (acetonitrile), yield 436 mg (80%), mp. 236-238˚C; IR (KBr) ν: 3229 (NH), 3090 (Ar-CH), 2938-2923 (ali-CH), 1675 (C=O), 1613 (C=N), 1586 (Ar-C=C), 1527 and 1331 cm^{-1} (NO_2); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.08-1.98 (m, 10H, cyclohexyl-CH_2), 2.02-2.46 (m, 1H, cyclohexyl-CH), 4.35-4.36 (d, 1H, *J* = 4.11 Hz, thiazinanone-H6), 4.80-4.81 (d, 1H, *J* = 4.11 Hz, thiazinanone-H5), 6.62-6.70 (m, 2H, Ar-H), 6.84-6.92 (m, 2H, Ar-H), 7.04-7.46 (m, 6H, Ar-H), 7.71 (m, 1H, Ar-H), 8.32 (m, 1H, Ar-H), 9.10 (m, 1H, Ar-H), 11.00 (br, hydrazo-NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.74, 26.53, 29.78 (cyclohexyl-CH_2), 47.63, 47.91 (thiazinanone-CH6,5), 57.08 (cyclohexyl-CH), 115.93, 123.64, 128.04, 128.22, 128.71, 129.57, 130.25, 130.37, 130.77 (Ar-CH), 129.11, 133.38, 133.69, 137.96 (Ar-C), 144.59 (Ar-*C*-NH), 146.51 (C=N), 168.87 (C=O); MS (*m/z*): 545 (M^+, 51), 462 (43), 499 (28), 455 (39), 182 (100), 141 (68), 77 (91); Anal. Calcd. For $C_{28}H_{27}N_5O_5S$ (545.61): C, 61.64; H, 4.99; N, 12.84; S, 5.88. Found: C, 61.48; H, 4.83; N, 12.74; S, 5.75.

***(Z)-N'-*(2,4-dinitrophenyl)-2,3-diphenylacrylohydrazide (8).**

Yellow crystals (acetonitrile), yield 8-12%, mp. 168-169°C; IR (KBr) ν: 3247 (NH), 3130 (Ar-H), 2930 (ali-H), 1693 (C=O), 1591 (Ar-C=C), 1542 and 1334 cm^{-1} (NO_2); ^1H NMR (400 MHz, $CDCl_3$) δ: 6.42 (s, 1H, acryl-CH), 7.10-7.55 (m, 10H, Ar-H), 7.94 (m, 1H, Ar-H), 8.48 (br, 1H, NH), 9.04 (m, 1H, Ar-H), 9.43 (br, 1H, amide-NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 117.65, 123.18, 126.17, 127.52, 128.15, 128.26, 129.19, 129.38, 129.85 (Ar-CH), 133.68, 139.75 (C1 and C2-acrylohydrazide); 130.00, 134.34, 135.60, 137.80 (Ar-C); 145.10 (Ar-*C*-NH), 165.18 (C=O); MS (*m/z*): 404 (M^+, 100), 356 (23), 221 (26), 205 (13), 195 (18), 181 (32), 138 (20), 77 (41); Anal. Calcd. for $C_{21}H_{16}N_4O_5$ (404.38): C, 62.37; H, 3.99; N, 13.86. Found: C, 62.25; H, 3.86; N, 13.77.

Single crystal X-ray structure determination of 7a and 8:

Suitable crystals were obtained by recrystallization from acetonitrile. The single-crystal X-ray diffraction study were carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-Kα radiation (λ = 1.54178 Å). Direct Methods for **7a** (SHELXS-97) [23] and dual space methods for **8** (SHELXT) [24] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2) [25]. Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(N) free). Semi-empirical absorption corrections were applied. For **8** an extinction correction was applied. In **8** the 2,3-diphenylacrylo substituent is disordered (see cif-files for details).

Compound 7a: red crystals, $C_{29}H_{23}N_5O_5S$, *Mr* = 553.58, crystal size 0.24 × 0.06 × 0.02 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 19.9611(6) Å, b = 11.4148(4) Å, c = 10.9667(4) Å, β = 93.844(1)°, V = 2493.16(15) $Å^3$, Z = 4, ρ = 1.475 Mg/m^{-3}, μ(Cu-Kα) = 1.601 mm^{-1}, F(000) = 1152, 2□$_{max}$ = 144.2°, 21195 reflections, of which 4907 were independent (R_{int} = 0.030), 364 parameters, 1 restraint, R_1 = 0.046 (for 4478 $I > 2\sigma(I)$), wR_2 = 0.118 (all data), S = 1.08, largest diff. peak / hole = 0.723 / -0.490 e $Å^{-3}$.

Compound 8: yellow crystals, $C_{21}H_{16}N_4O_5 \cdot C_2H_6OS$, *Mr* = 482.50, crystal size 0.32 × 0.16 × 0.12 mm, triclinic, space group *P-1* (No. 2), a = 9.0191(3) Å, b = 11.3050(3) Å, c = 11.8112(3) Å, α = 87.986(1)°, β = 69.079(1)°, γ = 79.272(1)°, V = 1104.58(6) $Å^3$, Z = 2, ρ = 1.451 Mg/m^{-3}, μ(Cu-Kα) = 1.732 mm^{-1}, F(000) = 504, 2θ_{max} = 144.0°, 15897 reflections, of which 4309 were independent (R_{int} = 0.022), 313 parameters, 10 restraints, R_1 = 0.038 (for 4234 $I > 2\sigma(I)$), wR_2 = 0.093 (all data), S = 1.06, largest diff. peak / hole = 0.584 / -0.369 e $Å^{-3}$.

Supporting Information

CCDC 1840977 (**7a**), and 1840978 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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